Photoinduced Irreversible Effects on Magnetic Properties and Allied Phenomena in Magnetic Oxides. III

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I. Introduction

This review article is a continuation of the second previously reported paper[1] on the same title in which after effect connected with induced anisotropy, wall pinning by anisotropic ferrous ions, and optical absorption mechanism were described. The first observation of photoinduced changes in magnetic properties was reported by Teal *et al.*[2] in 1967. The authors used the ferromagnetic resonance technique to measure the anisotropy field of a single crystal of silicon doped yttrium iron garnet. The resonance field could be changed by infrared irradiation at low temperatures lower than 70 K. They explained the effect in terms of a redistribution of ferrous ions, Fe^{2+} over octahedral sites having slightly different energies owing to different orientation of the local symmetry axis with respect to the magnetization direction. Optical dichroism[3] and strain[4] are explained based on the same mechanism. These phenomena are designated as class-I effects. In these cases, the experiments were performed on single crystals of silicon-doped YIG with comparatively larger ferrous content $x=0.05-0.10$ per formula unit. On the other hand, the so-called class-II effects were discovered by Enz *et al.*[5] who observed the photoinduced changes in the permeability μ and coercive force H_c of YIG with very low content of Si less than 0.01 per formula unit. Infrared illumination was found to induce an irreversible decrease of μ and an increase of H_c so long as the low temperature is kept at e. g. 77 K. Due to a thermally activated relaxation process at temperatures about 120 K, the original state of the sample was brought back. This phenomenon may be explained in terms of an increase in a photoinduced pinning of domain wall although the microscopic origin of the photoinduced pinning center, however, has not yet been established. Demagnetization either after or during illumination has no influence on the lowered value of μ. This phenomenon is basically different from disaccommodation or development of time-dependent local induced magnetic anisotropy.[6] This review concerns with the main concept of photoinduced magnetic effects (*PME*) and intimately related problems.

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II. Photoinduced Magnetic Effects (*PME*) on Complex Permeabilities in Magnetic Oxides

2. 1 *PME* (White light) on μ in garnets and spinels

2. 1. 1 *PME* (Fe^{2+} center) in garnets

In this section, we discuss the experimental results belonging to the second class of the effect. As already mentioned, the first observation of this kind concerns *PKE* of the initial permeability μ of single crystalline and polycrystalline $Y_3\ Fe^{3+}{}_{5-3x}\ (Fe^{2+}\ Si^{4+})_x\ O_{12}$ with values of the silicon dope x in the range of 10^{-2}. Permeability μ is measured on toroids or picture frames by mutual inductance method at frequencies around 10 kHz and low drive fields ($\leqq$ 10mOe). A typical example is given in Fig. 1 ; after cooling to 77 K in the dark, on illumination by intense white light (10 mw/cm^2) the μ of YIG sample drops in a few seconds from its initial value of 120 to final value of 10. At temperatures below a certain threshold temperature T_r, this change in μ is irreversible. No influence of magnetic fields or the other wavelength light illumination so long as the authors have tried to renew illumination can bring back to the original high permeability state. For higher temperatures a relaxation towards the original state takes place after removal of the light. The threshold temperature T_r was reported about 200 K in polycrystalline YIG by Enz *et al.*[2], but 250 K in FZ YIG as discussed afterwards.[3] To examine the temperature dependence of *PME*, μ of Si-YIG ring was measured as a function of time both during and after irradiation with white light at various temperatures between 77 K and 300 K.[4] From these we can determine the megnitude of μ change or better of the change in the inverse susceptibility, χ the stiffness and the relaxation time after the light is switched off. The magnitude of change in χ decreases rapidly with temperature above 100 K. The relaxation time is determined from the slope of the μ vs. time curve immediately after switching of the light. Thus, both at the high low side of the temperature range studied, relaxation times are difficult to measure with sufficient precision as is seen clearly from the curve in Fig. 2. A plot of relaxation times against temperature seems to indicate a thermally activated behavior between 250 K and 170 K with an activation energy 0.2 eV. For lower temperatures the Enz's picture which will be discussed afterwards more in detail is less clear, but an activation energy is probably less than 0.05 ev. Recently the authors obtained the new results in the out of phase of initial permeability μ'' *vs.* temperature measurement and eliminated the ambiguity. In all measurements of the *PME* of μ at temperatures below 150K it was found that the magnetization stae of the samples during the illumination is not changed. Thus demagnetizing the sample after illumination does not change the value of μ ; even if the sample is magnetically saturated during illumination, the similar reduction of μ is found when it has been returned to the demagnetized state. These observations show that the change is

uniform through the volume of the sample and is not in any way connected with local magnetization direction during illumination. At these low temperatures it is also found experimentally that the change in μ depends only on the product of light intensity and time ; the effect is thus truly integrating. The magnitude of decrease was found to remain irreversible so long as the low temperature is maintained. A considerable number of related studies have to date been made, but in many of these studies, the inclusion in single crystal samples of impurities from the fiux or the crucible caused problems in a point of reproducibility. As a consequence, the research in this area has not been progressed as far as it was expected in the early stage. We give the results to show afterwards that the effect is quite general and not limited to some special property of YIG with a dopant of Si. A careful study of the donor centers, impurity and the ferrous ions Fe^{2+} content of polycrystalline and or single crystalline garnets showed that Fe^{2+} associated with oxygen vacancies are also effective in producing *PME* and for pure single crystal of YIG, oxygen vacancies are even the dominant donors.[5] The Fe^{2+} content of this material was found to be of the order of 10^{-3}. In YIG doped with Co^{2+} and Co^{3+} ions a *PME* of μ was observed at temperatures up to 0 °C, with only a slight magnitude of *PME*. The influence of other impurities in YIG was also studied. However, a direct evidence of contribution of other ions except Fe^{2+} is lacking or scarce. Of late, however, use of the floating zone method (FZ) is gradually making possible the growth of high purity YIG single crystals without relying on fluxes. Thus one interesting question has been whether this effect occurs in FZ YIG single crystal with silicon impurity contents reduced to negligible levels. On performing such experiments, the authors[6] have observed a prominent effect as shown in Fig. 3, and a noticeable change in tan δ or μ'' with illumination. Figure 4 represents the change in μ when the temperature of a sample was varied in the range from 77 K to 300 K. The upper part of the loop shows the measured result, whereas the lower part of the loop is for the sample heating after illumination at 77 K. The rate of both heating and cooling were approximately 100 K per hour. The effect of illumination on μ remains, to some extent, up to 260 K. Experimental results to date for polycrystalline YIG doped with silicon indicated that a change in μ remains up to about 210 K ; hence this limit is elevated to higher temperature by about 50 K in FZ-YIG

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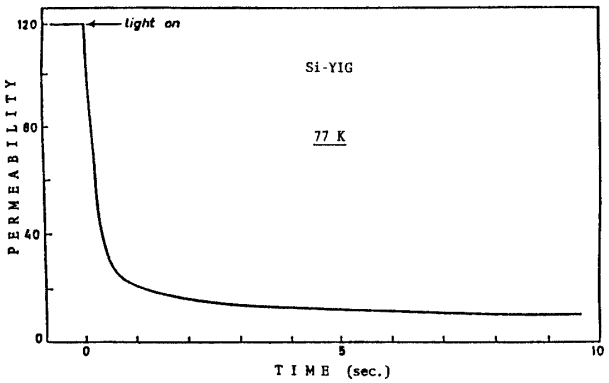

Fig. 1 *PME* of μ.[1)]

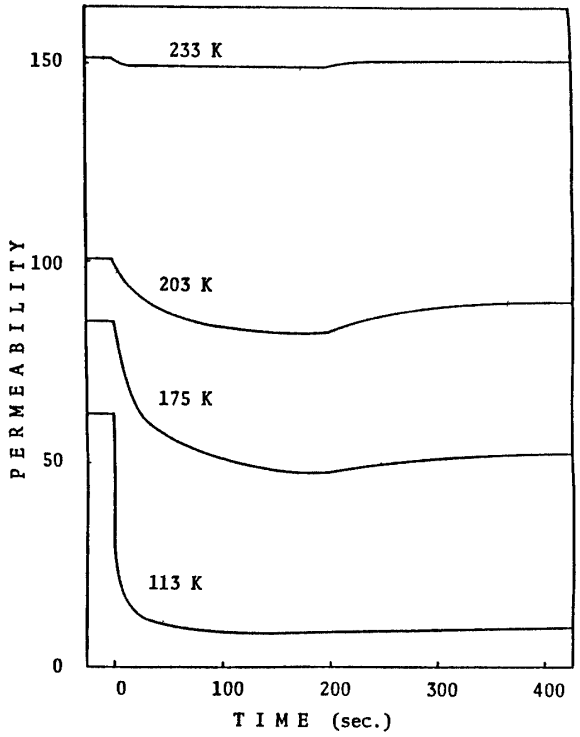

Fig. 2 *PME* of μ between 233 K and 113 K.[4)]

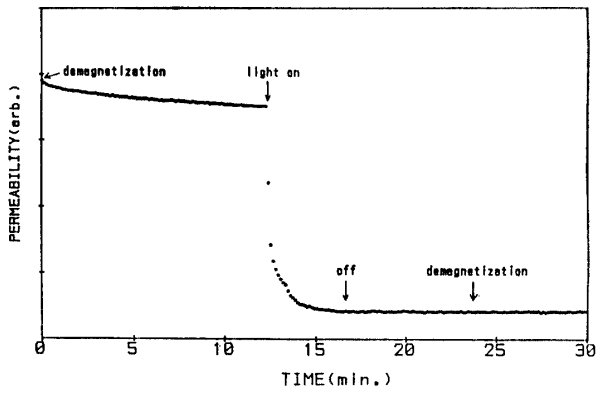

Fig. 3 Typical μ' vs. time curve of FZ YIG at 77 under illumination. Measuring frequency ; 1 kHz.[8)]

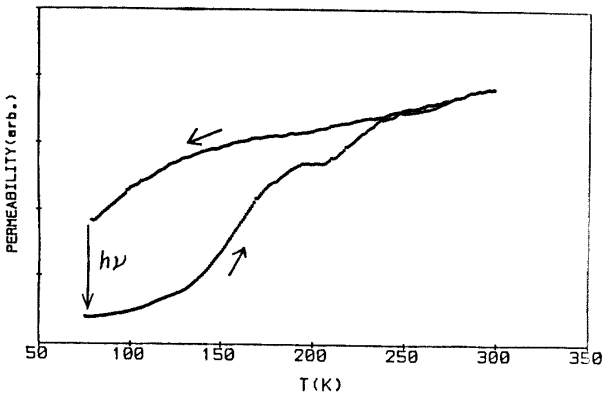

Fig. 4 Variation of μ' with a gradual change of temperature of FZ YIG sample before and after illumination at 77 K.[8)]

2. 1. 2 *PME* (Fe^{4+} center) in garnets

In the early stage of studying *PME* of μ' the authors found this effect also in YIG (Sr, Ca and or Pb)[1-4)] where these divalent additives are in excess of the maximum number of oxygen vacancies as shown in Fig. 1. To explain *PME*, a picture assumes that the uncompensated charge is weakly bound to the divalent ions and at low temperatures becomes localized at the tetrahedral sites to produce Fe^{4+} ion. It has been assumed that Fe^{4+} ions are homogeneously distributed on the tetrahedral sites and the magnetic behavior may be described in terms of five magnetic sublattices ; (a) Fe^{3+} at octahedral sites, (b) Fe^{3+} at tetrahedral sites (c) Fe^{2+} at octahedral sites, (d) Fe^{2+} at tetrahedral sites, (e) Fe^{4+} at tetrahedral sites. In this case, however, it is assumed to exist much more Fe^{4+} than the other ions. Because of the spin-orbit coupling of the Fe^{4+} ion, which has been energetically investigated in the single ion model for $3d^4$ ions by Rudowicz *et al.*[5,6)] For Fe^{4+}, the lowest free ion term is the ^5D term with $S=2$ and it is well separated from the next excited term by about 1.2 eV. The degeneracy for the ^5D term is lifted by the cubic

and the tetragonal distortions of the divalent ion-doped YIG structure and the leval splittings Δ_1, Δ_2, Δ_3, are shown in Fig. 2 (a). It has been suggested[6] that for spin $s>2$, fourth-order terms must be included in the spin Hamiltonian with the ζ axis along the $\langle 001 \rangle$ direction is given as

$$H_{spn} = B_o^{(2)} O_o^{(2)} + B_o^{(4)} O_o^{(2)} + B_d^{(2)} [O_{+d}^{(4)} + O_{-d}^{(4)}] \mu_B H_g S, \quad (1)$$

where $B_o^{(2)}$ anp $B_d^{(4)}$ are the constants that depend on spin-orbit coupling and the energy level splitting and $O^{(4)}$ (S) are the spherical tensor operators of the spin angular momentum (S). The spin Hamiltonian is transformed to a coordinate system ζ, Bz (H_{ex}) by using the coordinate transformation.[6] The energy levels E_{ms} are calculated in the second order perturbation theory with H_{spin} being the perturbation term to exchange Hamiltonian H_d, by evaluating the matrix elements of the transformed H_{spin} in the basis the eigenstates $\{S=2, M_s>\}$ quantized along the z axis and are given as

$$E_{ms} = E_{ms'} + E_{ms''} \quad (2)$$

where $E_{ms'}$ is symmetry independent and $E_{ms''}$ is a tetragonal symmetry-dependent energy term. The free energy of the single $3d^4$ or Fe^{4+} ion is

$$f = kT \ln \{ \sum_{Ms=-2}^{+2} \exp(-E_{ms}) \} \quad (3)$$

is obtained as

$$f_k(y) = f_{ok}(y) + f'_k(y) + f''_k(y) \quad (4)$$

where $f_{ok}(y)$ is the free energy part that is independent of the direction of the magnetization ; k represents one of the [001] directions and $y=\exp(-H_d'/kT)$. The free energy for the $<111>$ direction can be found by averaging over the free energy for the different inequivalent [001] directions. The cubic anisotropy energy K_1 and K_2 can then be written in the form[6]

$$K_1(T) = A_1(T) + A_2(T) + A_3(T) + A_4(T) \quad (5)$$

$$K_2(A) = P_1(T) + P_2(T), \quad (6)$$

The expressions for $A_1 \cdots\cdots A_3$ and P_i have been derived first by Cz. Rudowicz *et al.*[5,6] in Fe^{4+} ions in garnets. The assumption of the energy scheme in Fig. 2 (b) leads for $h = 200\ cm^{-1}$ to $A_1 = -0.158$, $A_2 = -0.090$ and $P_1 = 0.051$ and $P_1 = 0.002$ (in cm^{-1}/ion) and A_3 and A_4 are negligible. However, the only experimental data indicates that K_1 is small and positive.[7] Contrary to the ground singlet model,[6] the doublet model gives $K_1 = -85\ cm^{-1}$/ion and $K_2 = -250\ cm^{-1}$/ion. The predicted values of K_1 and K_2 can be useful for a Fe^{4+} ion with singlet ground state in other tetrahedral circumstances and prove the large role of the fourth order contribution A_2. Recently, Pardavi-Horváth *et al.*[8] found the *PME* in $Y_{2.01}$ $Ca_{0.99}$ $Fe_{4.10}$ $Ge_{0.90}$ O_{12} film. Depending on the sample coposition, there is a maximum temperature for the occurrence of the effect. The process occurs in three steps. Initially, a rapid decrease of the susceptibility χ with a time constant on the order of minutes is observed, as shown in Fig. 3, followed by a process when χ remains constant for several hours, and finally it decreases to its saturation value. They discussed the results in detail based on the idea that the local anisotropy can be changed drastically due to the presence of Fe^{4+} ions with a high spin-orbit coupling and high single-ion anisotropy.[9] If there are two or more inequivalent Fe^{4+} sites, and the energy supplied by the light quanta is enough to induce transitions between these sites then the domain walls will move towards the new minimum-energy positions, determined by the change in the wall energy profile.

As shown already, the Ca ions occupy dodecahedral sites which have tetrahedral Fe neighbors, two near but orientationally inequivalent sites at a distance of 0.31 nm and four far sites at 0.38 nm. If the concentration of the Ca^{2+} ions is not too high, the charge compensating Fe^{4+} ions will be located at nearest-neighbor tetrahedral sites, with an energy of E_1, forming Ca^{2+} -Fe^{4+} centers due to the Coulomb attraction. Upon illumination, the extra hole can be excited to another site having a higher energy, $E_1 > E_2$, due to local symmetry changes and the increased Ca^{2+} -Fe^{4+} distance. As a consequence, the anisotropy energy, the domain-wall energy, the coercivity, and χ will change. The first and fast process of the light excitation is related to the hopping of the hole between the two nearest-neighbor tetrahedral iron sites to the Ca impurity, a process essentially equivalent to the YIG (Si) described in the former section. The next process is the slow excitation of holes to nonmagnetic centers. The final state is reached through the creation of Fe^{4+} ions at far centers.

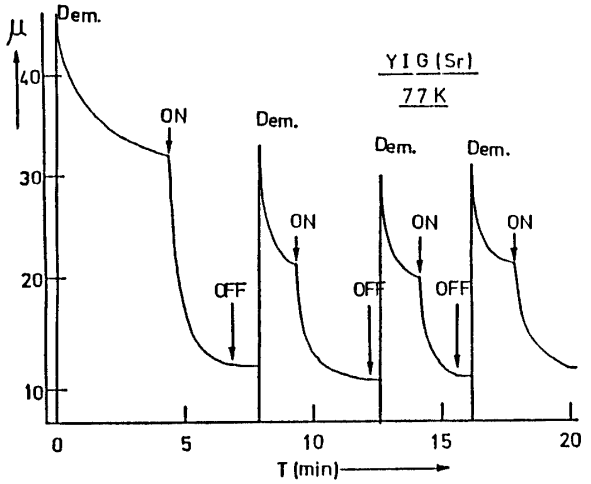

Fig. 1 *PME* of μ at 77 K for single crystal of $Y_{2.97}$ $Ss_{0.03}$ Fe_5 O_{12}.[4]

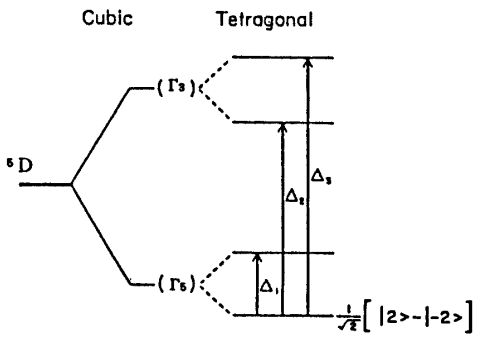

Fig. 2 (a) Crystal field splitting for tetrahedral Fe^{4+} in CaGe : YIG.

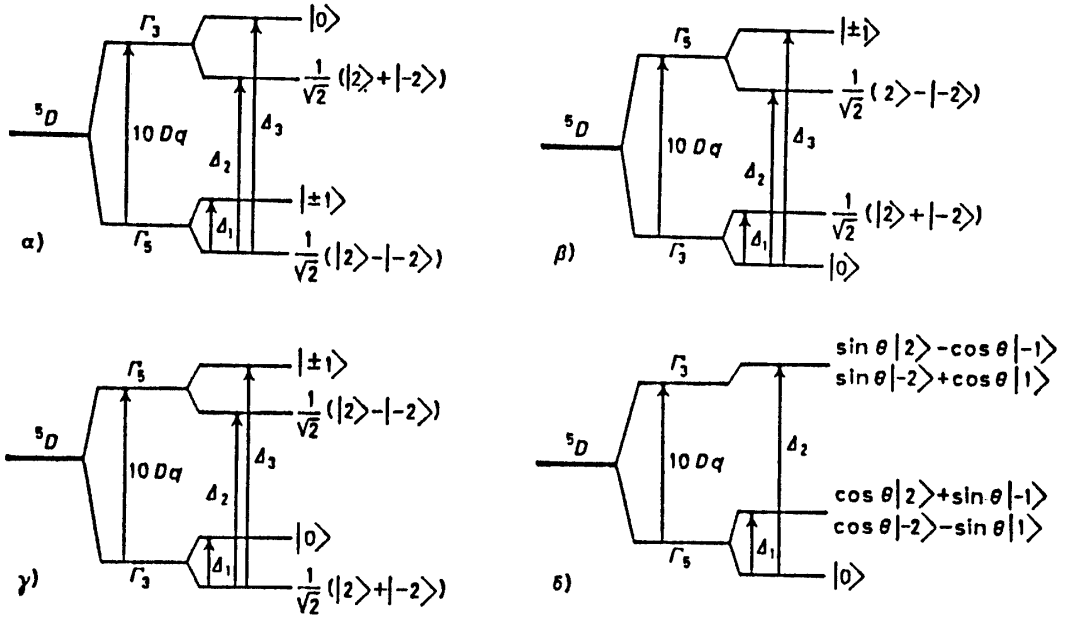

Fig. 2 (b) Ground-orbital-singlet energy level structures of a $3d^4$ ($3d^6$) ion in octahedral and/or tetrahedral crystal field axial distortion. α) d^4 : H_{tctr} ; d^6 : H_{oct} : V_{cf} ($\langle 001 \rangle$). β) d^4 : H_{oct} ; d^6 : H_{tetr} ; V_{cf} ($\langle 001 \rangle$). ν) d^4 : H_{oct} ; H_{tetr} ; V_{ef} ($\langle 001 \rangle$). δ) d^4 : H_{tetr} ; d^6 : H_{oct} ; V_{cf} ($\langle 111 \rangle$).[5]

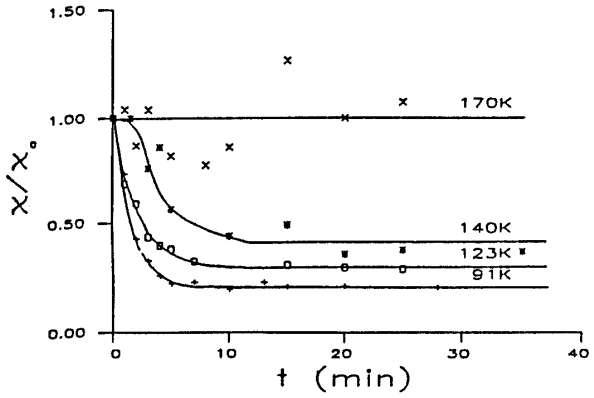

Fig. 3. Initial process of the time evolution of the initial susceptibility of $Y_{2.01}$ $Ca_{0.99}$ $Fe_{4.10}$ O_{12} film upon excitation with white light of 10 mW/cm^2 intensity.[8)]

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2. 1. 3. Temperature dependence of *PME* in garnets

As mentioned above, *PME* is only observable at low temperature, which is a serious obstacle to application. Based on the two center model[1)], the *PME* in YIG can be attributed to a following process, e. g.,

$[Fe^{2+}$ – Vacancy (O), or $Si^{4+}] + h\nu \rightarrow Fe^{2+}$ + Vacancy (O) or $(Si^{4+}) + E_{thermal} \rightarrow$

$[Fe^{2+}$ – Vacancy (O) $(Si^{4+})]$

From this relationship, a rate equation for an excitation of the form

$$dn/dt = -\alpha n^2 + \beta I (n_o - n), \qquad (1)$$

where n is the number of vacant number of centers and n_o the number of total number of centers at $t = 0$, I the light intensity, α a temperature dependent relaxation –rate coefficient, and β a wave-dependent sensitivity[2)] The recombination process may be thermally activated, which leads to a well known relation ;

$$\alpha = \alpha_o \exp(-E_a / kT). \qquad (2)$$

To describe the experimental results we need a relation between the concentration n and the measured magnetic properties, e. g.

$$\Delta(\chi^{-1}) = \chi^{-1}_{ill} - \chi^{-1}_{dark}. \qquad (3)$$

For concentrations below a critical concentration n_o the relation may be described

$$\Delta(\chi^{-1}) \propto n, \; n < n_c ; \qquad (4)$$

for higher concentrations

$$\Delta(\chi^{-1}) \propto n^{1/2}, \quad n > n_c \qquad (5)$$

In undoped YIG these relations were found to give a satisfactory description of the experiment[3]. For $t \geq 0$ the solution of eq. (1) is

$$n(t) = 2n_0 \{1+z \coth (\frac{1}{2} \beta I z t)^{-1},\} \qquad (6)$$

with

$$z = (1+4\alpha n_0 (\beta I)^{-1})^{1/2}$$

The explicit representation of solution is checked by one of the authors (K. M) ; a solution may be also found in Ref. 4. An analysis of $n(t)$ is rather complicated, however, since the factor β increases rapidly in the wavelength region where the absorption constant increases.[2] In practice this means that we have to work with an inhomogeneous intensity distribution in our samples. We preferred to illuminate the sample until a saturation value was reached and then analyse the relaxation curve. From Eq. 1 it follows that the saturation concentration n_s of the vacant centers is given by

$$n_s = 2n_o/(1+z) \qquad (7)$$

After the light is switched off, the relxation is described by

$$n(t) = n_s/(1+n_s t). \qquad (8)$$

The initial slope of the relaxation curve is

$$dn(t)/dt \mid_{t=0} = -\alpha n_s^2 \qquad (9)$$

To analyse the susceptibility behavior it is convenient to define the quantity

$$q = -1/\Delta(\chi^{-1}) \{d/dt\Delta(\chi^{-1})\}_{t=0} = (d\chi_{III}/dt)_{t=0} \chi_{dark}/\chi_{III}(\chi_{dark}-\chi_{III}). \qquad (10)$$

Substituting Eq. 10 together with Eq. 3 or Eq. 9 we find

$$q=\alpha n_s \text{ or } q=1/2\ \alpha n_s. \qquad (11)$$

The quantity q is a measure for the relaxation time of the *PME*.[5] It is demonstrated successfully as shown in Fig. 1.

We can distinguish the two limiting cases:

(1) When $\alpha n_o \leq \beta I$, we have $z \simeq 1$ or $n_s \simeq n_o$; this will be the case at low temperatures. With Eq. 3a we then get $q=\alpha n_o$; with Eq. 4 we get $q=1\text{-}2\ \alpha n_o$. In both cases the temperature dependence of q is given by

$$q \propto \exp(-E\alpha/kT) \qquad (12)$$

(2) When $\alpha n_o \geq \beta I$, we have

$$z \simeq 2(n_o/\beta I)^{1/2} \text{ or } n_s \simeq (\beta I n_o/\alpha)^{1/2}. \qquad (13)$$

This will be the high-temperature limit. Irrespective of whether Eq. 4 or 5 holds, the temperature dependence of q will be

$$q \propto \exp(-E\alpha/2kT). \qquad (14)$$

Erom the slope of this curve in the temperature region 77–180 K they obtained $E_\beta \simeq 0.08$ eV assuming that they were dealing with the low-temperature limiting case. For the region around 150 K $< T <$ 250 K, they obtained 0.2 eV or 0.4 eV. The authors obtained E_I=0.1 eV and E_{II}=0.3 eV in FZ-YIG, corresponding to their data, respectively in such a different way as measuring the low temperature peak and the higher temperature peak in μ.

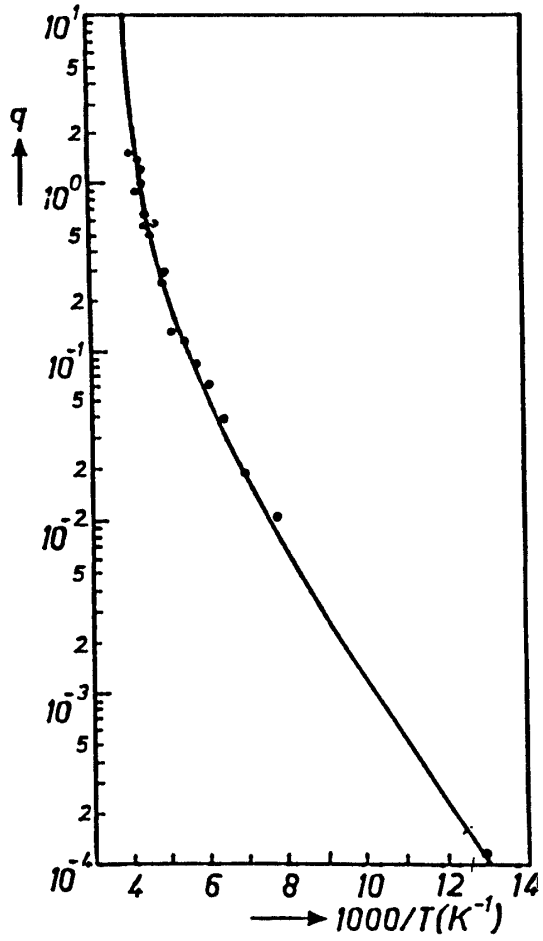

Fig. 1 The quantiy $q = \frac{\chi_{dark}}{(\chi_{dark}-\chi_{irr})\,\chi_{irr}} \left(\frac{d\chi_{irr}}{dt}\right)_{t=0}$ as a function of T^{-1} for a sample of $Y_3Fe_{4.75}In_{0.25}O_{12}$; q is a measure for the relaxation time of *PME*.[5]

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2. 1. 4 *PME* in coercive force and switching properties

Changes in domain wall behavior similar to the effect described in the previous section have been observed in the study of the shape of the hysteresis loop by Enz *et al.*[1] In Fig. 1, a typical change is shown for a polycrystalline ring of YIG (Si ; 0.006) : the loop becomes square upon illumination and H_c increases from 0.6 to 2.0 Oe. This change in the hysteresis properties is even more prominent when the high-speed switching measurements are carried out.[2] In Fig. 2 (a), the so-called *S*-curves at 4.2 K are plotted : these give the relative amount of flux switched by a square field pulse of amplitude H starting from a well-defined remanent state with the pulse duration as a parameter before illumination. The observed shape is similar to that of square-loop ferrites. As shown in Fig. 2 (b), upon illumination, a drastic change occurrs. In this experiment one can also define a dynamic coercive force H_c (τ) as the field necessary to switch half of the

remanent flux in time τ. The behavior of this coercive force under the illumination is very similar to that of μ H_c (μs) 77 K rises from a value of 1.4 Oe to 7.8 Oe after a long time of illumination. The relaxation behavior is also observable at 200 K. The increase of H_c (pulse width : 1μs)) is shown in Fig. 3 (a) and a relaxation time of the order of 70 sec as shown in Fig. 3 (b).

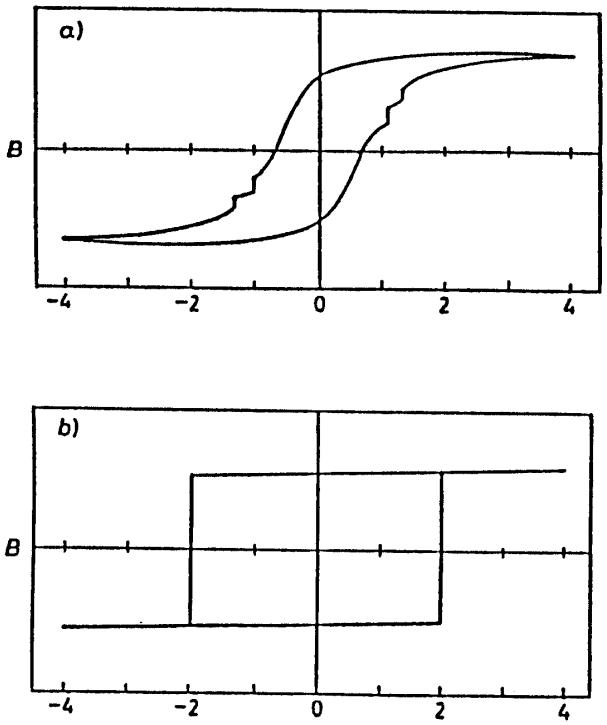

Fig. 1 Hysteresis loop of YIG ($Si_{0.006}$) at 50 Hz and 77 K a) after cooling in the dark b) after illumination.[1]

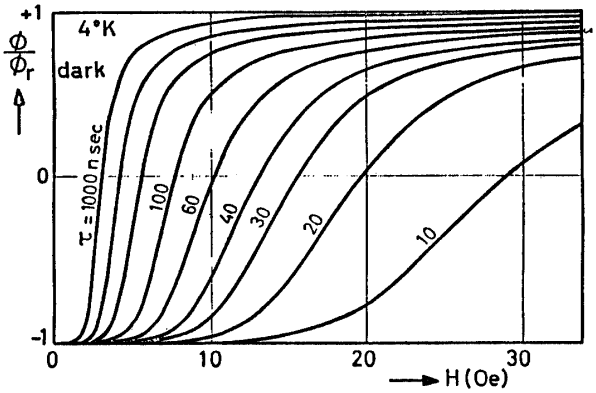

Fig. 2 (a) : In the dark.
Switehing behavior of YIG ($Si_{0.006}$) at 4.2 K. Amount of flux ϕ in units of the remanet flux ϕ_r switched by a field pulse of amplitude H[2]

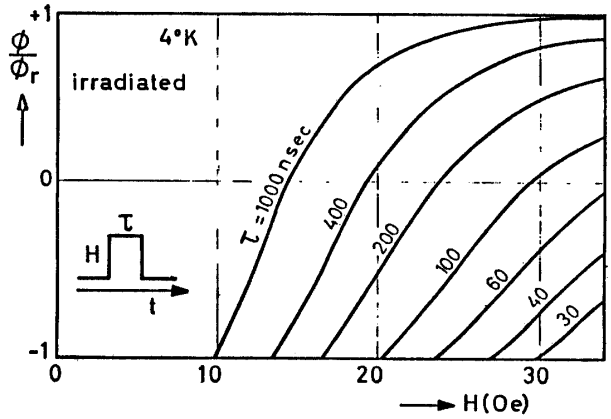

Fig. 2 (b) : After white light illumination.[2]

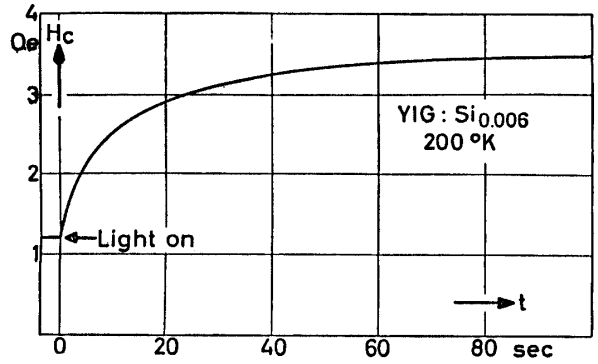

Fig. 3 (a) ; Light on.
Dynamie coercive force for 1 μs pulse H_c (1 μs) as a function t in YIG ($Si_{0.006}$) at 200 K.[2]

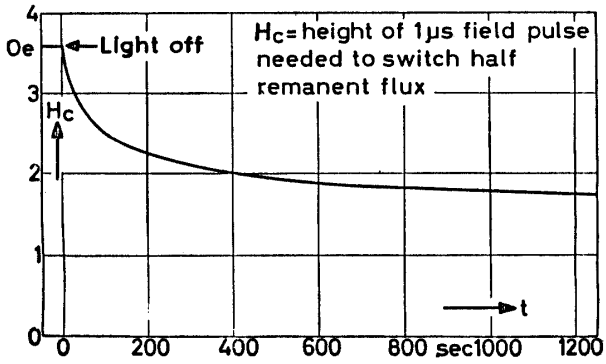

Fig. 3 (b) ; Switched off.

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2. 2 *PME* of μ in spinel ferrites and others

Only a few samples of spinel ferrite have been reported to show *PME*. The reason why only a few sample shows *PME* comparatively is not as yet clear. The one of the authors (K. H), however, would like to ascribe it to the larger attenuation of light than in YIG. The survey of these investigations is summarized in Table I. On the other hand Lems *et al.*[7] found a *PME* in Ga-doped $CdCr_2Se_4$ This sample has the the spinel structure and is ferromagnetic below 130 K.[8] The chemical formula of the sample is of the type

$Cd_{1-x}^{2+}Ga_x^{3+}Cr_{2-x}^{3+}Cr_x^{2+}Se_4$, $x=0.015$.

As shown in Fig. 1, μ falls off when light is switched on, whereas μ recovers when light is switched off, The relaxation time is of the order of a few seconds. Contrast to garnets, the experiment in this sample affords a good opportunity to check the two center model since μ recovers at 77 K upon switching off.

Lacklison *et al.*[9] found a *PME* in iron borate ($FeBO_3$). One of the authors (K. H) followed their experiments but the success has not been gained, which suggests the processing condition of the sample is very delicate.

Composition	$\Delta\mu/\mu$ at 77 K	References
$LiFe_5O_8$:Ru	~ 60%	Jonker[1]
$(NiZn)_1Fe_2O_4$:Co	~ 20%	Merceron, Holtwijk[2-3]
$LiFe_5O_8$:Co, Si	~ 60%	Hisatake[4]
$MgFe_2O_4$:Co	~ 40%	Hisatake[5]
Li-ferrite:Mn	~ 3.5%	Marais[6]

Table 1 *PME* in spinel ferrites

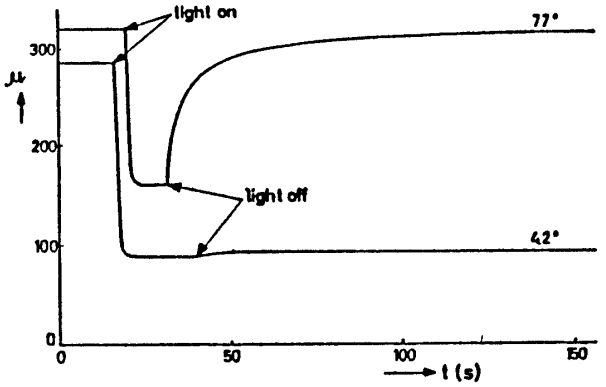

Fig. 1 Changes in μ for $CdCr_2Se_4 : Ga_{0.015}$ as a function of time t at T=77 K and 4.2 K.[7]

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2. 3 *PME* of Magnetic Loss

Permeability μ is defined as the ratio of the flux density induced in a material to the applying magnetic field. In an alternating magnetic field, however, the induced flux will not be in phase with the field because of losses, origin of which is not always simple. It is then convenient to define a complex permeability.[1]

$$\mu = \frac{B_0 \exp i(wt-\delta)}{H_0 \exp i(wt)} = \mu' - \mu'' \qquad (1)$$

At any value of the magnetic field as $H_0 \exp i(wt)$, the flux density will be delayed by some phase angle δ and its value will be given by $B_0 \exp i(wt-\delta)$. In phase with H, the μ can then be reduced to a real term, μ', which is therefore the normal permeability. An imaginary term μ'' contains the component of B that is 90° out of phase with H and therefore is a measure of the loss per cycle. The loss factor of a material is usually expressed by

$$\tan\delta = \mu''/\mu' \qquad (2)$$

In undoped YIG, the frequency dependence of μ' at several different temperatures is shown in Fig. 1, while the frepuency dependence of μ'' is in Fig. 2. If Fe^{2+} or Fe^{4+} ions are to be found in octahedral or tetrahedral sites only, an electron transfer process between two such sites may be essentially considered : The free energy of the Fe^{2+} ion, octahedrally coordinated, can be expected to be magnetically anisotropic ; if this is the case, the diffusing electrons will be available to them a number of sites of which energies depend on the orientation of the magnetization. Since the various octahedral sites in the garnet are not equivalent, we may expect that for a particular orientation of the magnetization, certain of these sites will be preferred to others. At thermodynamic equilibrium the electrons may then be distributed in a certain manner over the various sites, the distribution being governed by the orientation of magnetization and temperature. When the magnetization is rotated, the equilibrium is disturbed and the effective temperature of the particle system correspondingly is increased. If conditions favor diffusion, the system may relax from the excited state to a new equilibrium state as shown in Fig. 3.[3] The phenomenological description of relation between relaxation time and μ in the relaxation process has been given in Appendix I. Recently the authors have found a distinct phenomenon related with *PME* of tan δ[3] in a single crystal of YIG produced by a floating zone method. In this section the experimental results will be given rather in detail. As shown in Fig. 4 (a) and (b), the unilluminated tan δ is very low, 0.01 over $0.1 \sim 50$ kHz and in the temperature range between 77 K and 300 K the slight peak is observed only in the lower temperature in FZ-YIG sample. However, the behavior of illuminated tan δ contrasts with the one mentioned above. It turns out that over $77 \sim 300$ K and $0.5 \sim 10$ kHz, the double peaks of tan δ are found Here, the peak at higher temperature is termed as P_{I} and the another peak at lower temperature P_{II}. Over 10 kHz, these douple peaks are found to be coalesced into single one. From a frequency dependence of each peak as shown in Fig. 5, the activation energies are obtained as $E_{\mathrm{I}}=0.28$ eV for P_{I} and $E_{\mathrm{II}}=0.10$ ev for P_{II}, respectively. In spite of unillumination, double peaks of polycrystal line YIG (Si ; 0.01) sample have been already observed by Wurlitzer *et al.*[4] ; the corresponding activation energy $E_{\mathrm{I}} = 0.38$ eV and the $E_{\mathrm{II}} = 0.02 \sim 0.1$ eV, respectively. Furthermore, the authors found an interesting behavior in the sample. As shown in Fig. 6 (a), a thermal

change of tan δ on warming again after the sample is heated up to 120 K, in which P_{II} is clearly seen to be reduced. In Fig. 6 (b), single peak is situated at 120 K after warming up to 160 K. So far the duration of illumination is long or strong enough for μ' to be decreased in a saturated way. As shown in Fig. 7, photoannealing duration for 10 sec insufficient to be saturated gives rise to only a single peak of tan δ even when the temperature is raised up to 300 K. As already described, adiffusion damping shows considerably in certain spinels and garnets containing small concentrations of Fe^{2+} ions. With the alternating fields, transfers by diffusion from one Fe^{2+} ion to another in an equivalent lattice position, which may exert a viscosity-like drag on the moving wall. The anisotropy energy of the Fe^{2+} ion depends on the trigonal distortion of the octahedral sites, the exchange field, and the spin-orbit interaction.[1] The single ion anisotropy coupled with proper concention of the nonequivalent sites will provide a plausible loss mechanism. However, it was previously reported that μ'' shows the two maxima as a function of frequency at the fixed temperature in ferrites.[6] The lower frequency maximum may be attributed to the effect of wall resonance, while the higher frequency maximum is due to a rotation resonance. It is, in our situation, possible that the low frequency maximum may correspond to the low temperature peak P_{II} and the high frequency maximum to the high temperature peak P_I. Unfortunately this is not beyond speculation. It is also possible to assume that a migration of Fe^{2+} ion, depending on the migrations among the near sites or the sites might give rise to the saparated μ'' peaks due to a difference of the thermal potential barrier height.[6] In this context, the authors would like to propose other four models for the explanations in this section.

(A) The peak P_{II} of tan δ in Fig. 4 is supposed to be caused by an electron migration among near octahedral sites with an alternating field, since they may be thought to be shallow traps with low activation energy than among far octahedral sites. Antonini *et al.*[8] have found that Fe^{2+} ions may occupy both octahedral and tetrahedral sites contrary to the preceding reports.[6] On warming, a migration of Fe^{2+} ion among far sites matches the frequency of applied alternating field, giving rise to P_I. Correspondingly, a single peak in Fig. 6 (b) suggests a mixed or coupled migration of Fe^{2+} ions among both sites. An observation of only a single peak under a poor illumination nearly corresponding to a P_{II} temperature range is interpretted by assuming an absence of far sites occupied by Fe^{2+} ions. However, recently the authors found it more natural to ascribe the origin of P_I based on the picture that a potential well should be lower but the potential barrier is higher among far sites than among near sites. The assumed situation is given in Fig. 8.[8]

(B) The next model is proposed, based on the assumption that the potential energy at the octahedral sites near the oxygen vacancy could be lowered than at those from it. This situation is illustrated in Fig. 9 (a)$\sim$(d).

(C) From the other point of viev, it may be possible that the activation energy of electrons from the single charged oxygen vacancies and from the double charged ones are different. The double peaks of μ'' could be ascribed to the mechanism. These models mentioned above have a difficulty to explain why the clear-cut or separated maxima of μ'' have ltaken' place irrespective of continuous distribution of activation energies involved in this process. In this point, the next model will be natural.

(D) The fourth model assumes that P_I may be ascribed to an electron migration

among octahedral sites and P_{II} among tetrahedral sites. It is plausible that the potential in the former site will be deeper than in the latter one.[8] The assumed situation is illustrated in Fig. 10.[4] So far the several possible underlying mechanisms have been discussed. However, much work will be required before the detailed features and assignments of the centers can be determined.

Note added in proof

More recently, the authors have noticed that the picture similar to the model mentioned above (D) two level potential systems, in the other field of study was proposed for the explanation of behavior in photoinduced metastable defects in hydrogenated amorphous silicon.[10]

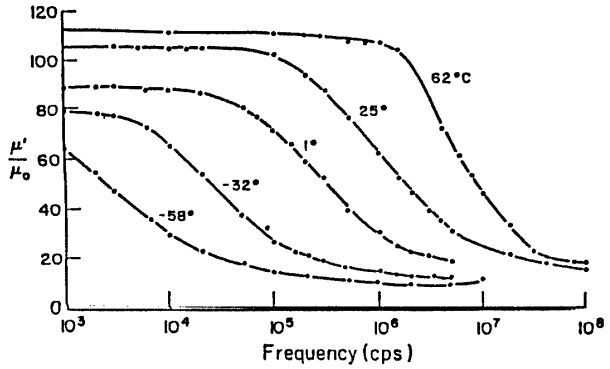


Fig. 1 μ' at several temperatures for a sample of YIG containing divalent irons.[2]

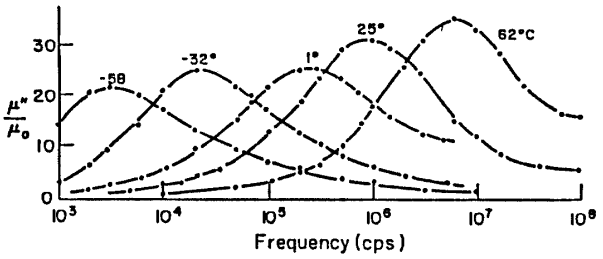


Fig. 2 μ'' at several temperatures for a sample of YIG containing divalent iron.[2]

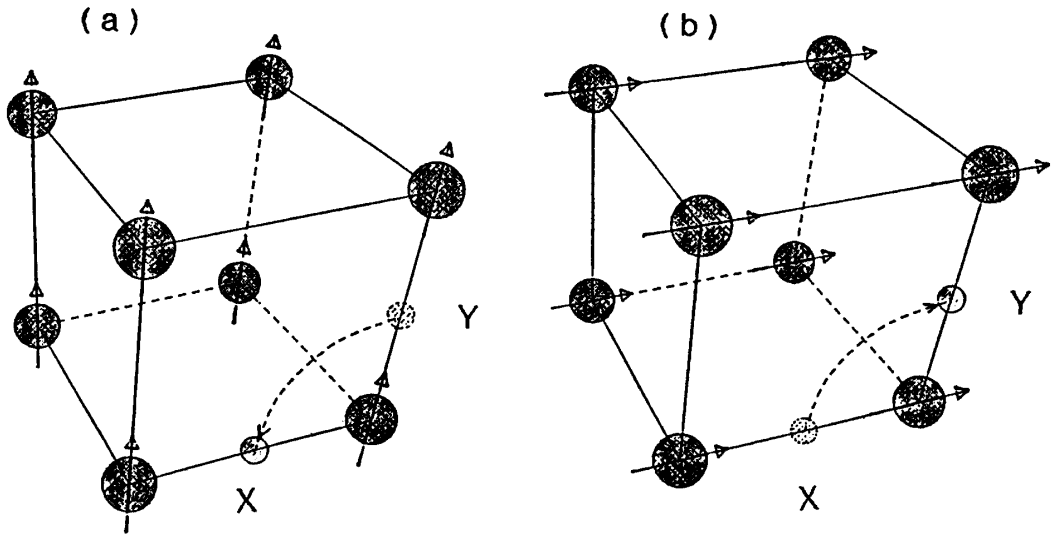


Fig. 3 Schematic representation of diffusion mechanism ; (a) system in equilibrium, (b) magnetization rotated to a new position and the particle system readjusted for a new equilibrium situation.[3]

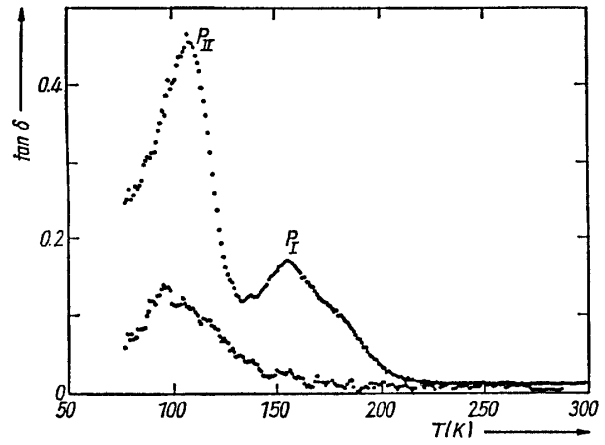


Fig. 4 (4) Thermal variation of tan δ of YIG sample at 2 kHz. The bottom curve is before and the top curve after illumination.[4]

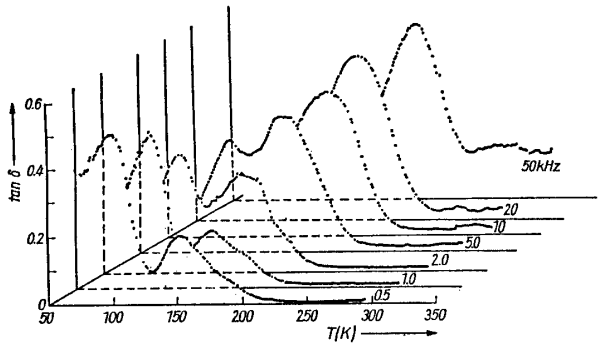


Fig. 4 (b) Thermal variation of tan δ with various frequencies after illumination.[4]

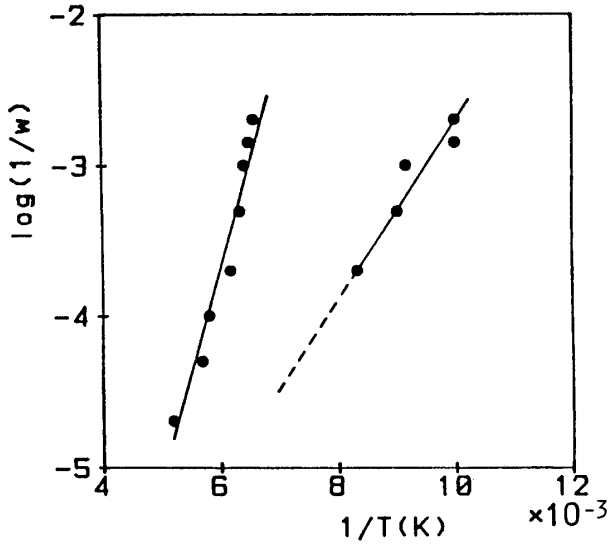


Fig. 5 Frequency dependenee of P_{I} (Left) and P_{II} (Right) temperature.

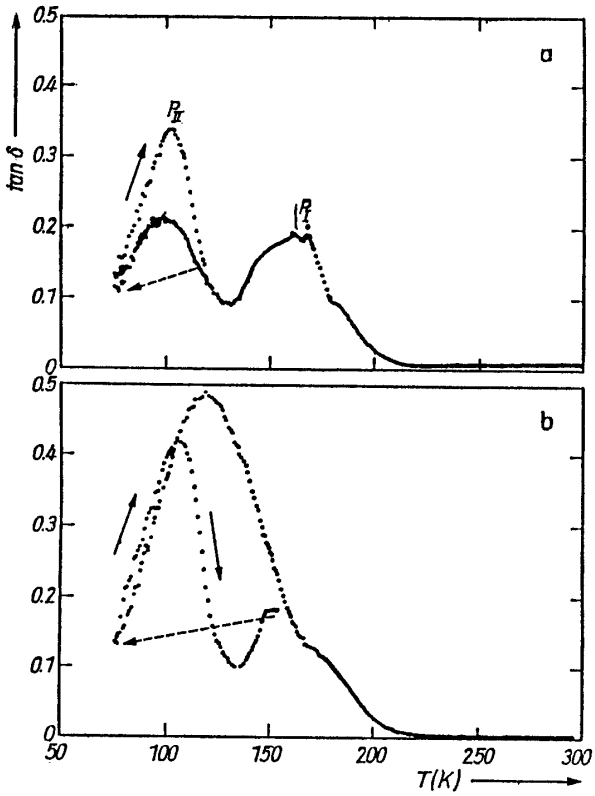


Fig. 6 Thermal variation of tan δ in the dark after illumination at 77 K a) Warming from 77 K again after warming to 120 K once, b) warming from 77 K again after warming to 169K (1 kHz).[4]

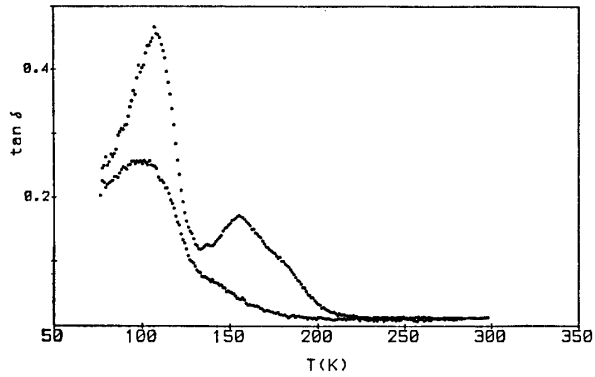


Fig. 7 Thermal variation of tan δ at 2 kHz. The bottom curve is after poor illumination and the top curve after full illumination.[7]

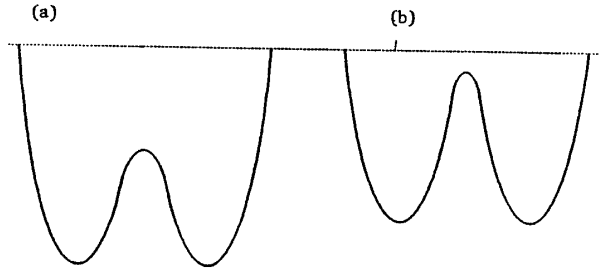
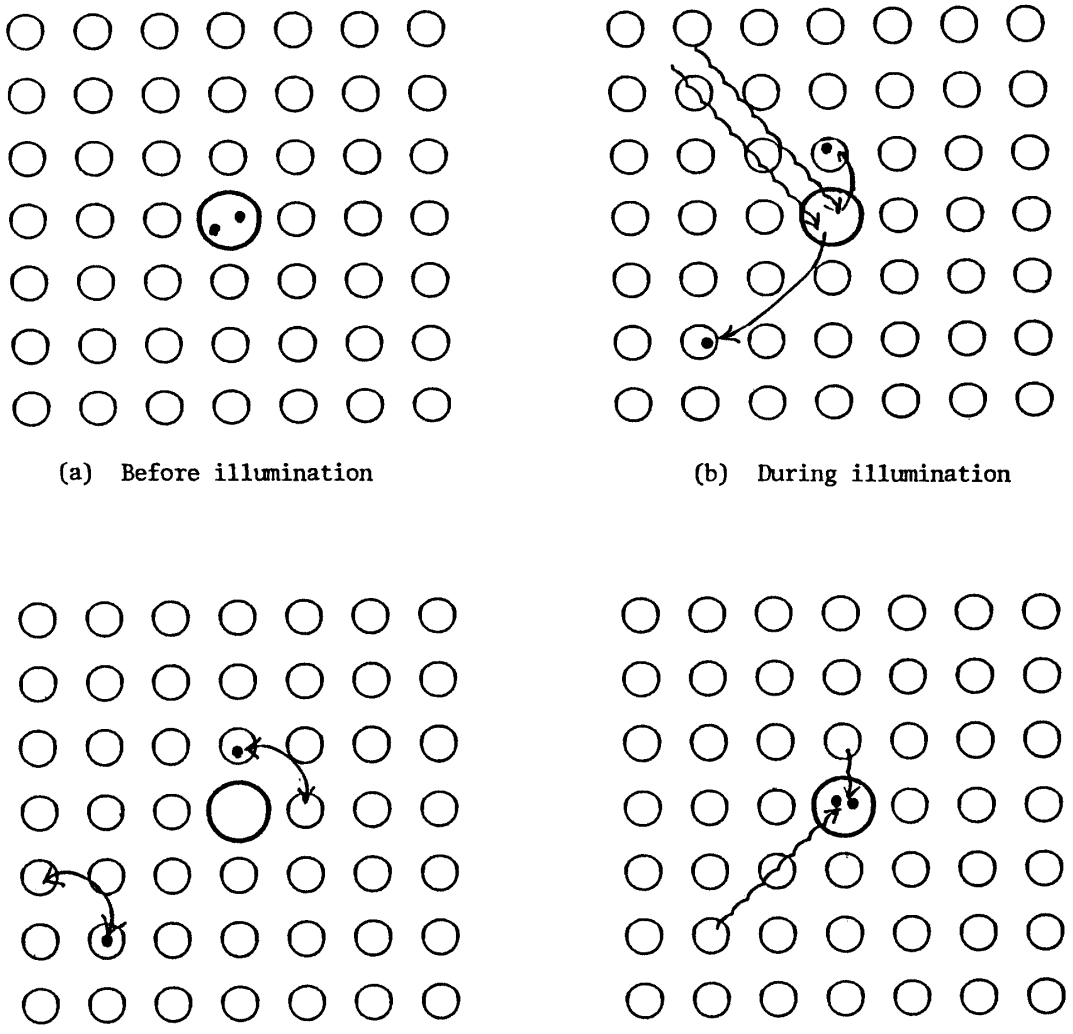


Fig. 8 Assumed potential scheme ; (a) near sites (b) far sites.



(a) Before illumination

(b) During illumination

(c) After illumination

(d) At high temperatures

Fig, 9 (a) - (d) Proposed mechanism in behavior of tan δ.9)

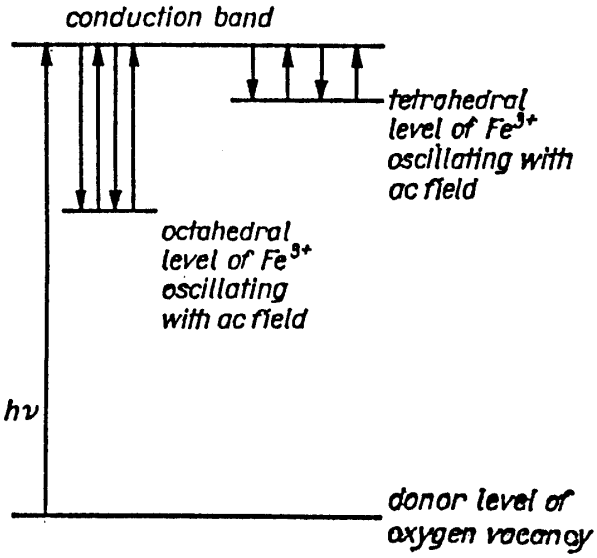


Fig. 10 10 Alternative schem of possible mechanism for double peaks of tan δ.4)

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2. 4 Relationship between *PME* and disaccommodation (*DA*)

As mentioned already, the induced preferred directions in the region of the Bloch walls create localized potential minima. As these minima become deeper with time, the mobility of the walls becomes more restricted, leading to a decrease in μ which is called disaccommodation (*DA*). Including *DA*, the behavior of the μ for diffcrent types of *PME* is surveyed in Fig. 1. In (a), *DA* is shown. After demagnetization (*D*), the domain wall configuration is such that it does not represent a situation of mimimum energy. If the thermal energy is sufficient, a spontaneous relaxation occurs. The experimentally measured time dependence of μ or *DA* especially in YIG[1] is well represented by the Richter function[2]

$$\mu(t) = \{\ln(t/\tau)\}^{-1} \int \exp(-t/\tau)\, d\ln(\tau) \qquad (1)$$

The Richter function corresponds to a material having a continuous distribution of relaxation time. The fraction of the material with a time constant between τ and $\tau + d\tau$ is $d\tau/\tau$ for $\tau_1 < \tau < \tau_2$ and none of the material has time constants outside this range. Often these are a very broad spectrum of activation energies and as a result μ falls linearly with the logarithm of t that has elapsed since the demagnetization. The specific property characteristic of *DA* is that demanetization brings back μ before decrease. In (B), *PME* of μ (Enz-type)[3] is shown at two different temperatures. In practice we have found combinations of *PME* and *DA* as shown in (C).[4] Apart from the observed results, it is possible if photoinduced local change takes place in the wall and causes a change in the wall and causes a change in the depth of the potential well that photoinduced *DA* may occur as shown in (D). Next we have to answer the question why *PME* and *DA* may respond to the demagnetization in different ways as mentioned above. In Fig. 2, we show pictorially the explanation of reason why μ is not sensitive to the demagnetization. In *PME* pinning centers may be assumed to distribute all over the sample when the long time has elapsed after illumination neglecting a thermal relaxation, while they may be localized within domain wall in *DA* process. It may be easily understood in this illustration that the state (B) may be equivalent to (D).

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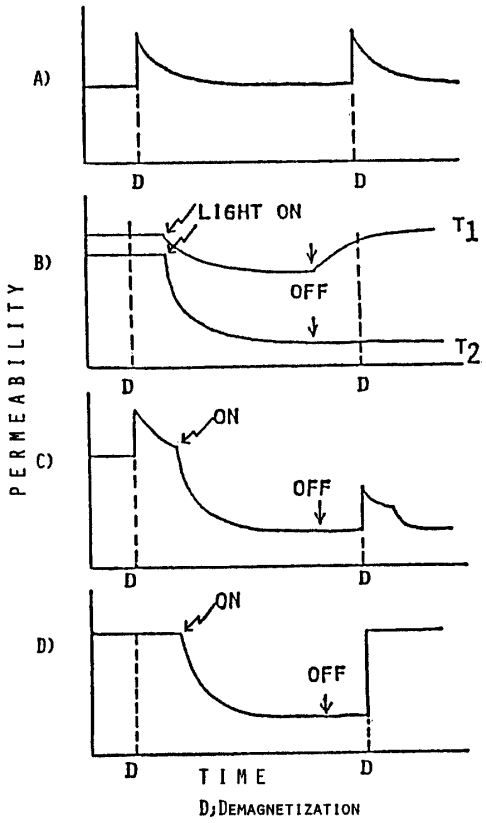
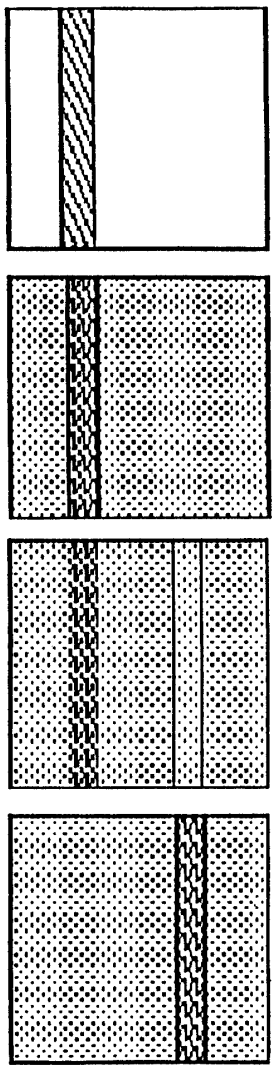


A) DA, B) PME (ENZ-TYPE), C) DA+PME, D) PHOTOINDUCED DA

Fig. 1 Types similar to *PME*.



a) Before illumination

b) After illumination

c) Just after demagnetization

d) Long after demagnetization

Fig. 2 Pictorial explanation of response in *PME* for demagnetization.

III Conclusive remarks in *PME* of μ

This review article has been concerned with the *PME* on μ mainly in yttrium iron garnet (YIG). In the first place, the pioneering work by Enz *et al.* was introduced and discussed.This is however, focused on an introduction to our study of the problems since our work is now being in progress. A photoinduced decrease in μ' is observed over 90 % at 77 K in the highly pure single crystal of YIG grown by a floating zone method. Furthermore, μ'' is found to show an increase unlike μ' on illumination at 77 K and on warming the double peaks below 10 kHz. From the frequency dependence of these peaks, the activation energies obtained are 0.1 and 0.3 eV, respectively.The peak at lower temperature shows a maximum, whereas the other peak at higher temperature shows a monotonic increase with the strength of illumination. Furthermore, this phenomenon is found reproducible when a gamma-ray or visible or near infrared laser was used in place of

white light illumination. The results will be reported in the forthcoming issue of this series.

The study of *PME* proved exciting and stimulating to a diverse array of fields that span the range from the basic solid state physics, physics of magnetism, physics of optical process to applications of magnetic materials and the magnetic devices. Very recently, one of the authors (K. H) has been informed by T. Yamashita[1] of the suggestion that optical process in a high temperature superconducting material may be intimately related to *PME* and the recent works by Masumi *et al.*[2~6] will have an impact on our study. In a near future it is possible to develop our study for an application of superconducting process.

Note added in proof

Very recently we observed the three maxima of μ'' in YIG (Ga) between 77 K and 300 K.[7]

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Appendix I : Relation between temperature and activation energy in relaxation process.

The relaxation process may be described by the postulation that after the application of a magnetic field H the magnetization M does not immediately reach its final equilibrium value M. In the simple way, the change of magnetization may be assumed to be proportional to its deviation from the equilibrium value :

$$dM/dt=1/\tau(M'-M) \qquad \text{(A. 1)}$$

The change of M with time is then given by an exponential function :

$$M=\{1-\exp(-t/\tau)\}M' \qquad \text{(A. 2)}$$

In an alternating field $H=H_0\exp(i\omega t)$ and χ' is defined by the relation $M'=\chi' H$. Then the accompanying magnetization is

$$M=\chi' H/(1+j\omega\tau) \qquad \text{(A. 3)}$$

From these equations, μ' and μ'' follow as

$$\mu'=1+4\ \pi\chi'/(1+\omega^2\tau^2),$$
$$\mu''=1+4\ \pi\chi'\omega\tau/(1+\omega^2\tau^2). \qquad \text{(A. 4)}$$

The relation between relaxation time τ and temperature T may be described generally by the equation,

$$\tau=\tau_\infty\exp(E/kT) \qquad \text{(A. 5)}$$

where τ_∞ is the relaxation time at an infinite temperature and E is the activation energy in this process. The equations μ' and μ'' may be expressed as the function of frequency and T ;

$$\mu'=1+4\,\pi\chi'/(1+\omega^2\tau_\infty^2\exp 2E/kT), \qquad \text{(A. 6)}$$
$$\mu''=4\pi\chi'\omega\tau/(1+\omega^2{}_\infty\tau^2\exp 2E/kT).$$

From the second equation in (A. 6), the maximum of μ'' has been given at the temperature T,

$$T=2E/\{k\ln(1/\omega^2\tau_\infty^2)\} \qquad \text{(A. 7)}$$